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Synthesis of a multifunctional alkoxysiloxane oligomer

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An alkoxysiloxane oligomer (**1**, SiMe[OSi(CH=CH$_2$)(OMe)$_2$][OSi(CH$_2$)$_3$Cl(OMe)$_2$]$_2$), containing vinyl and chloropropyl groups, was synthesized as a precursor for sol-gel synthesis. Di-*tert*-butoxymethylhydroxysilane (*t*-BuO)$_2$MeSiOH was reacted with ClSi(CH=CH$_2$)(OMe)$_2$ to form (*t*-BuO)$_2$MeSiOSiCH=CH$_2$(OMe)$_2$ which was further alkoxysilylated with Cl(CH$_2$)$_3$SiCl(OMe)$_2$ to form **1**. The ^{1}H, ^{13}C, ^{29}Si NMR and HR-MS data confirmed the formation of **1**, indicating the successful synthesis of an alkoxysiloxane oligomer possessing different kinds of functional groups by a chemoselective route. Hydrolysis of **1** under acidic conditions was completed in a few hours. The solution state ^{29}Si NMR spectra of samples hydrolyzed and condensed at various reaction times show no signals due to species generated by the cleavage of the siloxane bonds in **1,** indicating the validity of the synthesized substance as a precursor for the formation of hybrids with homogeneously distributed functional groups. Intramolecular condensation of **1** to form cyclic trisiloxane units proceeds more preferentially than intermolecular condensation.

1. Introduction

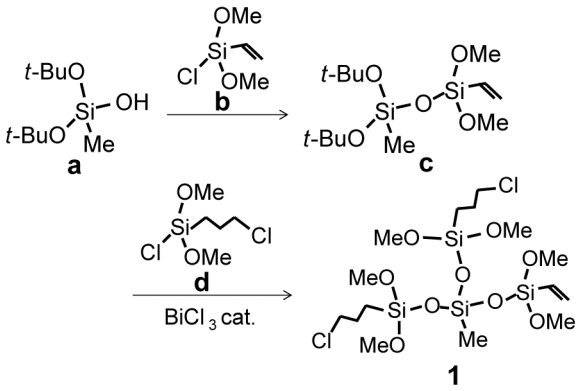
Silica-based inorganic-organic hybrid materials have been studied for applications in many fields.[1] Their properties are affected by functional group diversity, distribution, and the separation or distance between individual functional groups. For example, bifunctional catalysts like acid-base catalysts, show higher catalytic activity than monofunctional catalysts because of cooperativity between acidic and basic sites.[2] In addition, the catalytic activity is generally affected by the change in the distribution and separation between two kinds of functional groups.[3,4] However, it is difficult to control the distribution and/or separation between different kinds of functional groups by conventional methods for preparing hybrids, such as post-grafting[5] and co-condensation using sol-gel methods.[6] Inhomogeneous distributions of functional groups may be induced by post-grafting. Such heterogeneity also results from different rates of reaction between precursors (mainly mixtures of organoalkoxysilanes and tetraalkoxysilane) by co-condensation methods.

To overcome this problem, it is reasonable to use a well-designed oligomer as hybrid precursors because the separation and number of functional groups can be fixed at the molecular level for such oligomers. Therefore, one expects to control the distribution and/or separation between functional groups in hybrids by using oligomers as single precursors.[7] Alkoxysiloxane oligomers are suitable as building blocks of silica based inorganic-organic hybrids materials because they have hydrolyzable alkoxy groups. However, examples of alkoxysiloxane oligomers with defined structures are quite limited.[8-10] Furthermore, there are few examples that demonstrate the successful synthesis of compounds possessing both plural functional groups and alkoxysilyl groups.[11] In fact, a previous report[11] used the following two methods. One method uses stepwise synthesis of those compounds and the other does silylation of silanol-containing compounds with chlorosilanes possessing two kinds of functional groups. The former consists of hydrolysis of alkoxy groups and silylation of silanol groups. In this method, it is necessary to use a precursor that is resistant to hydrolysis, such as polyhedral silsesquioxanes (POSSs), to introduce plural functional groups in regioselective ways while retaining the oligosiloxane structure of the precursor. Thus, this approach is not versatile because of the limitation of available precursors. The latter uses chlorosilane possessing two kinds of functional groups for silylation of silanols allowing the synthesis of an alkoxysiloxane oligomer with different functional groups. However, the ratio and separation of the different functional groups is fixed, and it is difficult to control these factors by this method. Different from those reports, the present study shows stepwise introduction of plural different functional groups under non-hydrolytic conditions, and this method can control the ratio and distance of functional groups. Even though different functional groups can be bonded to polyhedral silsesquioxanes (POSSs),[12] such modified POSSs are not normally constructed with alkoxysilyl functional groups.

Recently, we reported non-hydrolytic synthesis of branched alkoxysiloxane oligomers (Scheme S1, Please see the Electronic Supplementary Information, ESI†).[13] Siloxane bonds can form by this method from alkoxysilyl groups which release stable carbocations, such a *t*-Bu$^+$ and Ph$_2$HC$^+$. Therefore, this approach offers the potential to control the structure and functional groups on the alkoxysiloxane oligomers by designing a precursor and selecting silylating agents. However, the synthesis of an oligomer with several kinds of functional groups has not yet been achieved.

Here, we report the synthesis of a typical oligomer having different functional groups (Scheme 1). In this work, we succeeded in designing and thereafter constructing an oligosiloxane structure with selected placement of functional groups. Chloropropyl and vinyl groups were chosen as functional

groups because these groups can be converted to catalytically active groups, including amino, thiol, and carboxy groups. In addition, the hydrolysis and condensation process was investigated by liquid state NMR to confirm the absence of siloxane bond cleavage of the oligomer. Because compound **1** (Scheme 1) retains the original oligosiloxane structure after condensation, the distribution and separation of functional groups in the resulting hybrids can be controlled by using **1** as a precursor.



Scheme 1 Synthesis of alkoxysiloxane oligomers.

2. Experimental

2.1 Materials

Acetonitrile (Wako Pure Chemical Co. Ltd., >99.0 %, dehydrated), bismuth chloride (Kanto Chemical Co. Ltd., >98.0 %), *tert*-butyl methyl ether (Wako Pure Chemical Co. Ltd., >99.0 %, dehydrated), (3-chloropropyl)trichlorosilane (Tokyo Kasei Co. Ltd., >97.0%), hexane (Wako Pure Chemical Co. Ltd., >95 %), 0.01 mol/L hydrochloric acid (Wako Pure Chemical Co. Ltd.), methanol (Wako Pure Chemical Co. Ltd., >99.8 %, dehydrated), potassium *tert*-butoxide (Tokyo Kasei Co. Ltd., >97.0%), pyridine (Wako Pure Chemical Co. Ltd., >99.5 %, dehydrated), sodium sulfate (Wako Pure Chemical Co. Ltd., >99.0 %, dehydrated), tetrahydrofuran (THF) (Wako Pure Chemical Co. Ltd., >99.5 %, dehydrated, stabilizer free), trichloromethylsilane (Tokyo Kasei Co. Ltd., >98.0%), and trichlorovinylsilane (Tokyo Kasei Co. Ltd., >98.0%) were used without further purification.

The following sections from 2.2 to 2.5 show brief summary of the synthesis of the compounds **a**, **b**, **c**, and **d**. The experimental details and full characterization data are shown in ESI† (Figs. S1-S6 for **a**, Figs. S7-S9 for **b**, Figs. S10-S12 for **c**, and Figs. S13-S15 for **d**.).

2.2 Synthesis of (*t*-BuO)$_2$MeSiOH (a).

Compound **a** ((*t*-BuO)$_2$MeSiOH) was synthesized from trichloromethylsilane. At first, trichloromethylsilane was alkoxylated with potassium *tert*-butoxide at room temperature, and it formed (*t*-BuO)$_2$MeSiCl. The remaining Cl did not react with the butoxide because of the steric hindrance of two *t*-BuO groups. Next, (*t*-BuO)$_2$MeSiCl was hydrolyzed with H_2O to synthesize **a**.

2.3 Synthesis of (MeO)$_2$(CH$_2$=CH)SiCl (b).

(MeO)$_2$(CH$_2$=CH)SiCl (**b**) was synthesized by the alkoxylation of trichlorovinylsilane with *tert*-butyl methyl ether as we previously reported[14].

2.4 Synthesis of (*t*-BuO)$_2$MeSiOSi(CH=CH$_2$)(OMe)$_2$ (c).

(*t*-BuO)$_2$MeSiOSi(CH=CH$_2$)(OMe)$_2$ (**c**) was synthesized by alkoxysilylation of **a** with **b**.

2.5 Synthesis of Cl(CH$_2$)$_3$SiCl(OMe)$_2$ (d).

Cl(CH$_2$)$_3$SiCl(OMe)$_2$ (**d**) was synthesized by the same way as **b**. (3-Chloropropyl)trichlorosilane was used instead of trichlorovinylsilane.

2.6 Synthesis of SiMe[OSi(CH=CH$_2$)(OMe)$_2$][OSi(CH$_2$)$_3$Cl(OMe)$_2$]$_2$ (1)

A solution of **c** (11.1 g, 32.2 mmol) in hexane (10 mL) was added to a solution of **d** and $BiCl_3$ in a 100 mL Schlenk flask. The molar ratio of **c** / **d** / $BiCl_3$ was 1/3/0.033. The mixture was stirred at room temperature for 24 h under N_2 atmosphere. Pyridine and methanol were added into the mixture and the mixture was stirred for 30 min for methoxylation of SiCl groups formed by functional group exchange reaction between **d** and **1**. After the completion of the reaction, confirmed by ^{1}H and ^{13}C NMR, the solvents, Cl(CH$_2$)$_3$Si(OMe)$_3$, *tert*-butyl chloride, remaining pyridine, and methanol were removed under reduced pressure. Then, colorless clear liquid **1** (4.1 g, 7.2 mmol, yield 23 %) was isolated by vacuum distillation after a solid residue was removed by filtration.

Compound 1. ^{1}H NMR (500 MHz; $CDCl_3$; 25 °C; TMS): δ = 0.27 (s, 3H), 0.75~0.78 (m, 4H), 1.86~1.91 (m, 4H), 3.50~3.53 (t, 4H), 3.55 (s, 12H), 3.56 (s, 6H), 5.85-5.92 (dd, 1H), 6.00-6.05 (dd, 1H), 6.12-6.16 ppm (dd, 1H) ; ^{13}C NMR (126 MHz; $CDCl_3$; 25 °C; TMS) δ = -3.2, 8.3, 26.4, 47.3, 50.30, 50.33, 128.9, 137.1 ppm ; ^{29}Si (99 MHz; $CDCl_3$; 25 °C; TMS) δ = -51.4 (2Si, T^1), -63.9 (1Si, T^1), -66.8 ppm (1Si, T^3)‡ ; HRMS (Electrospray Ionization, 2 kV) calcd. for $C_{15}H_{36}O_9Cl_2Si_4Na^+$ [M+Na]$^+$: 565.0707; found: 565.0706.

2.7 Hydrolysis and condensation of compound 1

Compound **1**, THF containing 10 vol% of THF-d_8, H_2O and HCl (0.01 mol/L) were mixed in a Teflon vessel and the mixture was stirred at room temperature. THF was used as the solvent because it is a compatible solvent for both compound **1** and H_2O.The molar ratio of compound **1**/THF/H_2O/HCl was 1/25/6/0.0005. Hydrolysis and condensation behaviors of the oligomer were investigated by constantly following the evolution of the relevant ^{13}C and ^{29}Si NMR signals. The details of the measurements are described in the characterization section.

2.8 Characterization

Solution ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on a Bruker AVANCE 500 spectrometer with resonance frequencies of 500.0 MHz, 125.7 MHz, and 99.3 MHz, respectively, at ambient temperature. Sample solutions were put in 5 mm glass tubes. The chemical shifts were referenced to internal tetramethylsilane (TMS) at 0 ppm. $CDCl_3$ and THF containing 10% of THF-d_8 were used to obtain lock signals. A small amount of Cr(acac)$_3$ (acac = acetylacetonate) was also added as a relaxation agent for ^{29}Si nuclei. ^{13}C NMR was measured with a recycle delay of 2 s and accumulations of 64 FIDs. ^{29}Si NMR was measured with a recycle delay of 10 s and accumulations of 64 FIDs for quantitative analyses. HR-ESI mass analysis was carried out with a JEOL JMS-T100 CS instrument. Samples were dissolved in methanol.

3. Results and discussion

3.1 Characterization of compound 1

The ^{1}H NMR spectrum of compound **1** (Fig. 1 (a)) shows nine signals at 0.27 (-Si*Me*), 0.75~0.78 (-Si-C*H*$_2$-CH$_2$-CH$_2$-Cl), 1.86~1.91 (-Si-CH$_2$-C*H*$_2$-CH$_2$-Cl), 3.50~3.53 (-Si-CH$_2$-CH$_2$-C*H*$_2$-Cl), 3.55 (-Si-(CH$_2$)$_3$Cl(O*Me*)$_2$), 3.56 (-Si-(CH$_2$=CH)(O*Me*)$_2$), 5.85-5.92 (-C*H*=CH$_2$), 6.00-6.05 (-CH=C*H*$_2$ (*cis* position to Si)), and 6.12-6.16 ppm (-CH=C*H*$_2$ (*trans* position to Si)). The integration ratio of these signals is 1.0 : 1.0 : 1.0 : 20.7 (containing all the signals at 3.50 ~ 3.56 ppm because of the overlapping) : 3.8 : 3.8 : 3.0 and these correspond to the calculated ratio (1 : 1 : 1 : 22 : 4 : 4 : 3). On the other hand, there are no signals assigned to *t*-BuO groups of the compound **c** (*t*-BuO)$_2$MeSiOSi(CH=CH$_2$)(OMe)$_2$.

These results indicate the alkoxysilylation accompanied with complete elimination of *t*-BuO groups. Furthermore, vinyl and chloropropyl groups are retained without any side reactions. The ^{13}C NMR spectrum (Fig. 1 (b)) also shows the presence of chloropropyl and vinyl groups and the absence of *t*-BuO groups, which strongly supports this conclusion.

The ^{29}Si NMR spectrum of compound **1** (Fig. 1 (c)) shows three signals at -51.4, -63.9 and -66.8 ppm and their intensity ratio is 1.9 : 1.1 : 1.0. The singlet signal at -51.4 ppm is assigned to -*Si*(CH$_2$)$_3$Cl, because the number of -*Si*(CH$_2$)$_3$Cl group is twice as that of -*Si*(CH=CH$_2$) or -*Si*Me groups. The other two signals at -63.9 and -66.8 ppm are assigned to -*Si*^{T1}(CH=CH$_2$) and -*Si*^{T3}Me, respectively, because of the following two reasons. i) The signal due to T^1 Si atoms possessing vinyl groups appears around -62 ppm.[15] ii) The signal due to T^3 Si atoms possessing methyl groups appears around -65 ppm.[16] These assignments are also supported by a computational analysis. The details on the method are shown in ref. 17. The results show that the signal due to Si of Si^{T3}-methyl group appears at higher magnetic field by 4.02 ppm than that due to Si of Si^{T1}-vinyl group. As mentioned above, the measured signal due to Si of Si^{T3}-methyl appeared at higher magnetic field by 2.9 ppm than that due to Si of Si^{T1}-vinyl. The high-resolution ESI-MS spectrum shows a peak at *m/z* = 565.0706 corresponding to [M+Na$^+$] (calcd. mass: 565.0707). These results confirmed the synthesis of compound **1**.

Therefore, it is successful to synthesize the siloxane oligomer which has alkoxy groups and plural functional groups. It is reasonably expected to synthesize siloxane oligomers which possess both acidic and basic functional groups by transforming the vinyl and chloropropyl groups of **1**, respectively. In addition, alkoxysiloxane oligomers which have other functional groups can be synthesized by changing the kind of alkoxychlorosilanes under the same reaction processes. Furthermore, the ratio of functional groups can be controlled by changing the order of the alkoxysilylation. Because alkoxychlorosilanes are easily synthesized from chlorosilanes, the synthetic method presented here is very versatile.

3.2 Hydrolysis and condensation of compound 1.

The solution ^{13}C NMR spectra of compound **1** hydrolyzed for different reaction times (Fig. 2) indicate the complete hydrolysis between 2 - 3 h after the beginning of the reaction. Please note that the chemical shifts of ^{13}C NMR signals in Fig. 2(0 h) were slightly different from those in Fig. 1 (b) because THF-d_8 was used to obtain the spectra of Fig. 2 (0 h) while $CDCl_3$ was used for the spectrum of Fig. 1 (b). THF-d_8 was chosen because THF is compatible with both **1** and H_2O.

The signal intensity assigned to methoxy group (50.4 ppm) decreased steadily, and disappeared after 3 h. A new signal assigned to methanol simultaneously appeared at 49.7-49.8 ppm. In addition, all the signal intensities due to methyl (-3.1 ppm), vinyl (130.2 ppm and 136.4 ppm) and 3-chloropropyl groups (9.0 ppm, 27.4 ppm, and 47.8 ppm) of compound **1** are weakened with the time course of hydrolysis and condensation, while many new signals for the same functional groups appearing at chemical shifts similar to those for compound **1** (The magnified spectra are shown in Fig. S16, ESI†). These results are interpreted to mean that the environments of the carbon atoms of those groups change as hydrolysis and condensation progresses. The diversification of the environments is caused by the following factors. i) Because compound **1** contains hydrolysable six -SiOMe groups, very many kinds of molecules will be generated by hydrolysis of **1**. ii) In the condensation process, two kinds of cyclic siloxane will be formed by intramolecular condensation (Scheme 2), and the stereoisomers will be generated when these molecules are formed. Detailed interpretation and assignments of ^{13}C NMR signals are shown in ESI†.

Multiple signals are observed in the ^{29}Si NMR spectra (Fig. 3) of hydrolyzed solutions of compound **1**, and assignments of these signals are shown in Table 1. (Please note that the chemical shifts of ^{29}Si NMR signals in Fig. 3(0 h) were slightly different from those in Fig. 1 (c) because of the difference in deuterated solvent.) It is quite difficult to assign these signals precisely because their chemical shifts are very close together. Three signals appear at -49.9 ppm, -62.7 ppm, and -66.5 ppm in 0.5 h. As confirmed by the ^{13}C NMR (Fig. 2), the hydrolysis is complete within 2-3 h. Therefore, these signals are assigned to *Si*OH groups generated by hydrolysis (Scheme 2). These three signals disappear steadily after 2 h, and new signals appear at -49.7 ppm to -50.5 ppm, -56.9 ppm to -57.4 ppm, and -63.1 ppm to -63.9 ppm. We will discuss below the assignments of these signals to two types of molecules; i) molecules generated by cleavage of siloxane bonds of compound **1** or ii) molecules generated by intra- and inter-molecular condensation.

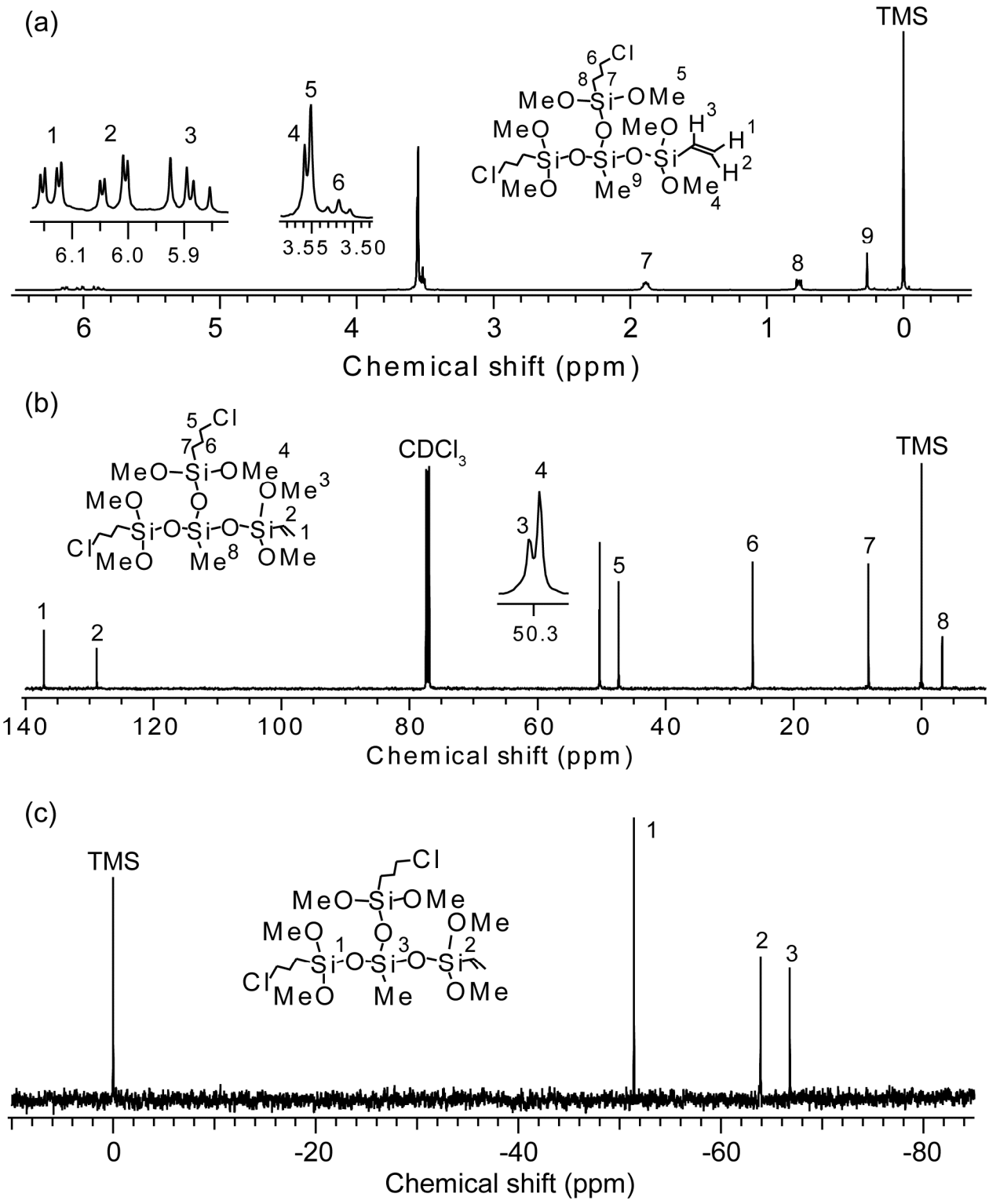


Fig. 1 Liquid state (a) ^{1}H, (b) ^{13}C and (c) ^{29}Si NMR spectra of **1** in $CDCl_3$.

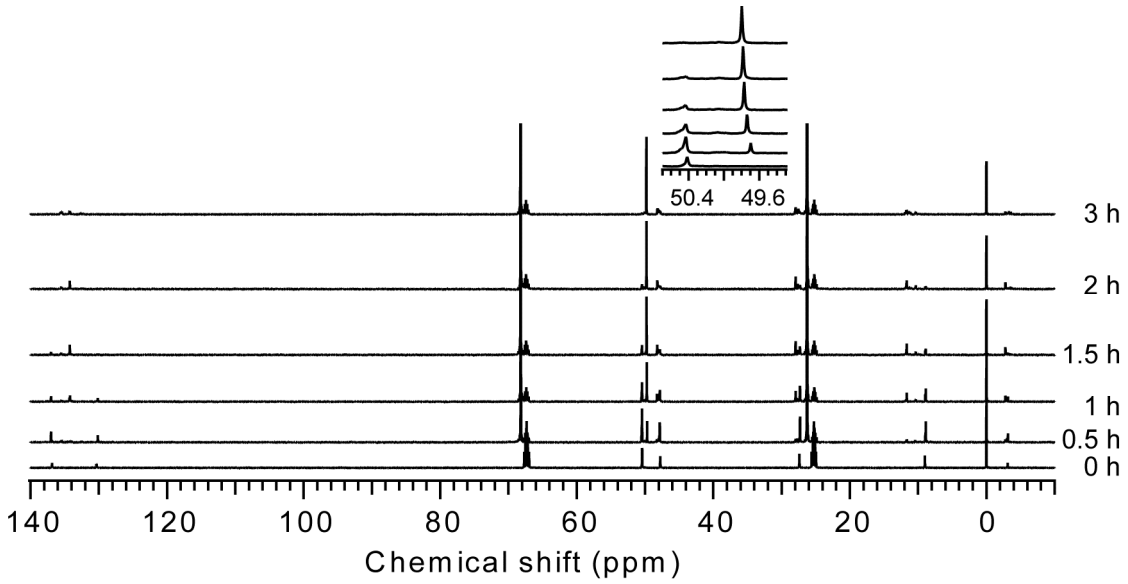


Fig. 2 ^{13}C NMR spectra (THF-d_8) of **1** hydrolyzed for 0 h, 0.5 h, 1 h, 1.5 h, 2 h, and 3 h.

Table 1 Assignments for ^{29}Si NMR signals of hydrolyzed **1**.

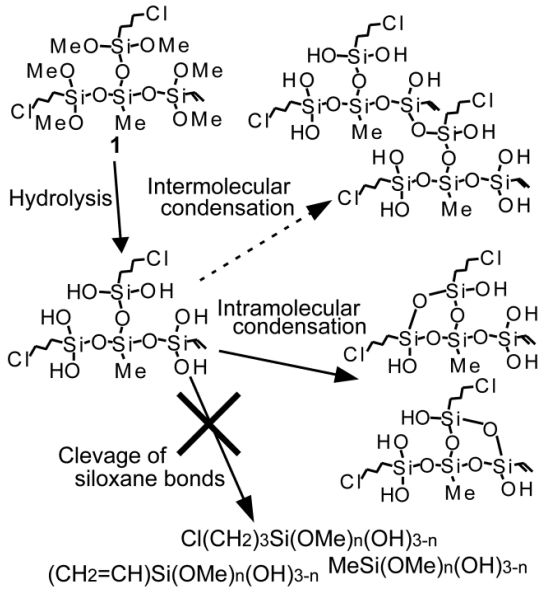
Time / h	- *Si*$(CH_2)_3Cl$	- *Si*$(CH{=}CH_2)$	- *Si*Me
0	$T^1_{(OMe)2}$: -51.4 ppm	$T^1_{(OMe)2}$: -64.3 ppm	$T^3_{(OSi)2}$: -66.7 ppm
0.5 - 1.5	$T^1_{(OH)2}$: -49.9 ppm	$T^1_{(OH)2}$: -62.7 ppm	$T^3_{(OSi)2}$: -66.5 ppm to -66.7 ppm
2 -10	$T^2_{OH,OSi,}$ $T^3_{(OSi)2}$: -49.7 ppm to -50.5 ppm	$T^2_{OH,OSi,}$ $T^3_{(OSi)2}$: -56.9 ppm to -57.4 ppm	$T^3_{(OSi)2}$: -63.1 ppm to -63.9 ppm

* Symbol T of T^n_x denotes three oxygen atoms on Si. The superscript n of T^n_x means the number of Si bonded to the central Si atom. The subscript x of T_x denotes the kind of functional groups linked to Si atom.

At first, the cleavage of siloxane bonds of compound **1** was examined. If the siloxane bonds of compound **1** are cleaved, $Cl(CH_2)_3Si(OMe)_n(OH)_{3-n}$, $MeSi(OMe)_n(OH)_{3-n}$ and $(CH_2{=}CH)Si(OMe)_n(OH)_{3-n}$ (n = 0~3) would be generated (Scheme 2). However, there are no signals in the T^0 region corresponding to these molecules (-36 ppm to -44 ppm, -52 ppm to -56 ppm, and -38 ppm to -40 ppm,[18] respectively). Because these molecules are easily observed under acidic conditions,[18] it is quite reasonable to conclude that the oligosiloxane structure of compound **1** is not degraded under the conditions used here.

Next, intramolecular condensation of compound **1** is discussed. The overlapped signals of the sample after the reaction for 2 h, appearing at -49.7 ppm to -50.5 ppm, -56.9 ppm to -57.4 ppm, and -63.1 ppm to -63.9 ppm, are assignable to -*Si*$(CH_2)_3Cl$, -*Si*$(CH{=}CH_2)$, and -*Si*Me of cyclotrisiloxanes, respectively (Table 1). *Intra*molecular condensation naturally forms cyclic siloxane structures and the terminal T^1 silicon atoms of compound **1** become T^2 silicon atoms. Signals corresponding to T^2 silicon atoms of cyclotrisiloxanes appear downfield from T^2 silicon atoms in non-cyclic compounds because of ring strain.[19] The presence of too many signals can be explained by the formation of two types of cyclic siloxanes (Scheme 2) and their geometric isomers.[20]

Finally, intermolecular condensation of compound **1** is discussed. The signals in the ranges from -56.9 ppm to -57.4 ppm and from -62.8 ppm to -63.9 ppm might be assigned to *inter*molecularly condensed species of compound **1**, in which the hydroxy groups of -*Si*$(OH)_2(CH_2)_3Cl$ are used for condensation (Scheme 2), because it is known that signals



Scheme 2 Proposed reaction processes for hydrolysis and condensation of compound **1**.

corresponding to T^2 and T^3 silicon atoms of intermolecularly condensed species appear upfield than T^1 silicon atoms.[19] However, there are no signals corresponding to intermolecularly condensed species derived by condensation of hydroxy groups of -$\underline{Si}(OH)_2(CH=CH_2)$ around at -80 ppm. The absence of species resulting from intermolecular condensation of -$\underline{Si}(OH)_2(CH=CH_2)$ group can be explained by the following two reasons. At first, the intensity of the signals due to –$\underline{Si}(OH)_2(CH=CH_2)$ is lower than that of -$\underline{Si}(OH)_2(CH_2)_3Cl$ because the number of -$\underline{Si}(CH=CH_2)$ group is half of -$\underline{Si}(CH_2)_3Cl$ group. Second, the signal intensity of each silicon atom is weakened because the environment of silicon atoms is diversified and the molecular mobility is decreased by intermolecular condensation. The same reasons can be applied to explain the absence of the signals assigned to -$\underline{Si}$Me groups after 3h. For these reasons, signals due to intermolecularly condensed species are normally observed to much lesser degrees. Therefore, we can not completely exclude the possibility of intermolecular condensation. However, the observed signals are clearly assigned as the progress of intramolecular condensation, which leads us to conclude that the last one proceeds preferentially rather than intermolecular condensation.

As shown above, the siloxane linkages are not broken, which indicates that the incorporated functional groups are located at the original positions. This means that the method presented here is quite useful for the design of precursors for the preparation of hybrid materials as well as mesostructured materials possessing functional groups distributed homogeneously with some fixed distance. This is superior to the grafting method[3] using two kinds of reagents, which provide hybrids with only locally distributed functional groups.

The preference of cyclization should be attributed to the branched oligosiloxane structure of compound **1**. In the case of linear oligosiloxane, it is reported that intramolecular condensation is competed with intermolecular condensation except for in a dilute solution.[21] In comparison with a linear oligosiloxane, silanol groups generated by hydrolysis of alkoxy groups of compound **1** are sterically close to one another. Therefore, it is quite reasonable that intramolecular condensation proceeds preferentially because silanol groups generated by hydrolysis of alkoxy groups are close to each other and condense easily. Cyclic siloxanes generated by intramolecular condensation possess four silanol groups which are not used for intramolecular condensation. After the formation of cyclic siloxanes, Si-O-Si networks can be constructed by intermolecular condensation among these silanols. The formation of Si-O-Si networks by intermolecular condensation should result in the broadening of NMR signals and the decrease in their intensities because the environment of Si atoms is diversified and the molecular mobility is decreased by the Si-O-Si network formation. In fact, the signals in the spectra of the products reacted for 10 h and 24 h after the beginning of hydrolysis were broadened and also the intensity of signals in those spectra decreased (Fig. 3). Hybrid materials prepared using branched oligomers are expected to possess unique features in terms of porosity and density because the position of silanol groups is so restricted that they are not able to react freely with neighboring silanol groups. The study on the relationship between the properties of hybrids and siloxane structures in various length scales is challenging for future design of siloxane-based materials.

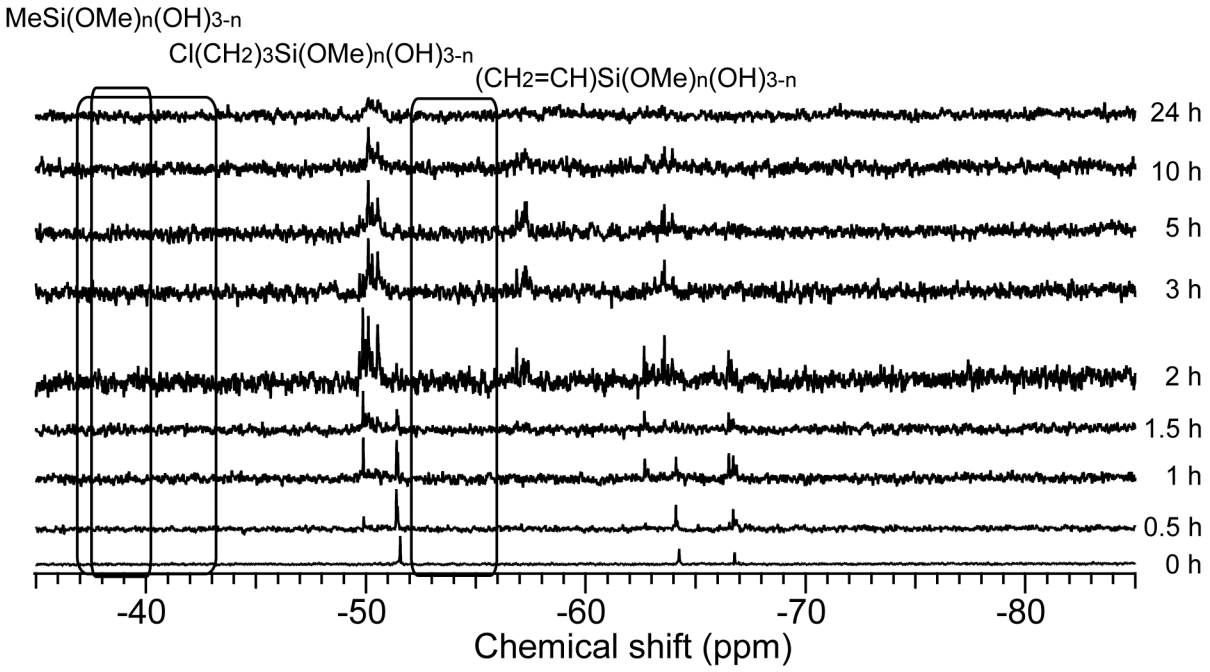


Fig.3 ^{29}Si NMR spectra (THF-d_8) of **1** hydrolyzed for different reaction times: 0 h, 0.5 h, 1 h, 1.5 h, 2 h, 3 h, 5 h, 10 h, and 24 h.

Conclusions

Alkoxysiloxane oligomer **1** possessing plural different functional groups has been successfully synthesized by combining a conventional silylation with non-hydrolytic silylation which does not involve the formation of silanol group during the reaction. The siloxane bonds are not cleaved during hydrolysis and condensation of compound **1**, as judged by ^{29}Si NMR data. It is indicated that intramolecular condensation proceeds more preferentially than intermolecular condensation. Therefore, compound **1** can be used as a building block to prepare hybrid materials via the sol-gel process. The distribution and separation between individual functional groups can be controlled by using this type of oligomer. Reactive functional groups are appended to vinyl and 3-chloropropyl group in this study. The extension of the kinds of functional groups that could be used to prepare hybrid materials with controlled functionalities will be a fruitful area of future research in sol-gel chemistry.

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Notes and references

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† Electronic Supplementary Information (ESI) available: See DOI: 10.1039/b000000x/

‡ Symbols of T^n denote bonding states of Si atom; T^n: $R_1\boldsymbol{Si}(OSi)_n(OR', OH, \text{or } O^-)_{3-n}$

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